

Balloon observations of organic and inorganic chlorine in the stratosphere: The role of HClO_4 production on sulfate aerosols

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Abstract. Simultaneous observations of stratospheric organic and inorganic chlorine were made in September 1993 out of Fort Sumner, New Mexico, using the JPL balloon-borne MkIV interferometer. Between 15 and 20 km, a significant fraction (20 - 60%) of the inorganic chlorine could not be accounted for by the sum of measured HCl , ClONO_2 , and HOCl . Laboratory measurements of the reaction of ClO radicals on sulfuric acid solutions have indicated that, along with HCl , small amounts of perchloric acid, HClO_4 , were formed. Very little is known about the fate of HClO_4 in the stratosphere and we use a photochemical box model to determine the impact of this new species on the partitioning of inorganic chlorine in the stratosphere. Assuming that HClO_4 is photochemically stable, it is shown that in the enhanced aerosol loading conditions resulting from Mt. Pinatubo's eruption, HClO_4 could represent a significant reservoir of chlorine in the lower stratosphere, sequestering up to 0.2 ppbv (or 50%) of the total inorganic chlorine at 16 km. The occurrence of this new species could bring to closure the inorganic chlorine budget deficiency made apparent by recent ER-2 aircraft *in situ* measurements of HCl .

Introduction

Once organic chlorine (CCl_y) has reached the stratosphere in the form of halocarbons, it is converted by photolysis and reaction with radicals to inorganic chlorine (Cl_y). Most of the inorganic chlorine species thought to play an important role in the stratosphere have been detected (HCl , ClONO_2 , HOCl , ClO , OClO), and a few others (Cl_2 , Cl , Cl_2O_2 , ClNO , ClNO_2) occur at abundances too small to be observable with current techniques. These compounds represent only a small subset of the many possible chlorine-containing compounds. In particular, higher oxides like ClO_3 , ClO_4 , Cl_2O , Cl_2O_7 , and oxo acids like HClO_2 , HClO_3 , HClO_4 have been characterized in the laboratory environment (Greenwood and Earnshaw, 1985), and their possible importance for stratospheric chemistry is still subject to speculation (Sander et al., 1989, 1995). As most of the higher oxides of chlorine tend to be unstable, they could be present in the stratosphere only in small quantities, but may possibly play an important role in the loss of stratospheric ozone (Prasad and Lee, 1994). On the other hand, if any oxo acid were to be formed under stratospheric conditions, it might be stable enough to constitute an important reservoir of chlorine.

In this paper, we first present evidence of a discrepancy in the chlorine budget as shown by MkIV balloon measurements in

September 1993. We then investigate the possible source of the missing chlorine, emphasizing a possible heterogeneous formation of HClO_4 . Finally we discuss the implications of the production of HClO_4 for the mid-latitude lower stratosphere in the context of the high aerosol loading conditions present after Mt. Pinatubo's eruption in 1991.

Missing Chlorine: MkIV observations

The MkIV interferometer is a Fourier Transform Infra-Red spectrometer (Toon, 1991), which has flown on 7 balloon flights since 1989 (Sen et al., 1996) as well as on several DC-8 campaigns. The set of measurements discussed here were taken on the flight of September 25, 1993, out of Fort Sumner, New Mexico. During this flight, an exceptionally clear tropopause allowed data to be taken nearly all the way down to the ground. The many gases measured between 5 and 39 km included species in the families of inorganic chlorine (HCl , ClONO_2 , HOCl), organic chlorine (CCl_3F , CCl_2F_2 , $\text{CCl}_2\text{FCClF}_2$, CHClF_2 , CH_3Cl , CCl_4), reactive nitrogen species, as well as tracers. In addition the Submillimeterwave Limb Sounder (Stachnik et al., 1992), on the same balloon payload, observed ClO simultaneously.

MkIV measures approximately 86% of the chlorine-bearing source gases. Adding to these gases an estimate of CH_3CCl_3 based on MkIV CFC-11 together with an empirical relationship between CH_3CCl_3 and CFC-11 (Elkins et al., 1996), we account for 99% of the organic chlorine in the troposphere (~ 3.8 ppbv; WMO, 1994). Furthermore, the sum $\text{ClONO}_2 + \text{HCl} + \text{HOCl} + \text{ClO}$ accounts for 82-100% of the total inorganic chlorine. We also

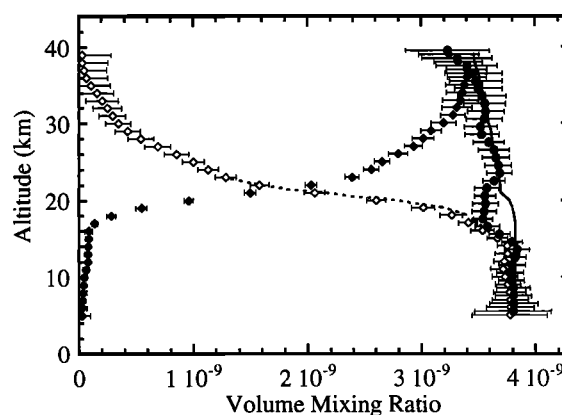


Figure 1. MkIV interferometer sunset measurements of organic (CCl_y : \diamond) and inorganic (Cl_y : \blacklozenge) chlorine on September 25, 1993 (34°N , 109.4°E). For better representation, the sum of observed Cl_y and CCl_y (\bullet) has been interpolated to a grid shifted by 0.5 km. The solid line is the calculated total chlorine based on the age of the air (see text). The dashed line shows the corresponding CCl_y as derived from the MkIV CFC-11 using empirical relationships determined from *in situ* organic chlorine observations aboard the ER-2.

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include estimates of COFCl (Sen et al., 1996) and of COCl₂ (Kindler et al., 1995). The resulting total organic and inorganic chlorine are presented in Fig. 1. [A more detailed description of these measurements and the data reduction used will be found in a forthcoming publication by G. Toon].

We compare the sum of measured Cl_y and CCl_y to the expected amount of total chlorine (Cl_t). Cl_t is a direct function of the age of the air (Woodbridge et al., 1995), which is calculated from the MkIV SF₆ measurements between 12 and 21 km, assuming a growth rate of 9% per year for SF₆ (WMO, 1994). For altitudes above 21 km where no reliable SF₆ mixing ratios could be retrieved, a linearly increasing age reaching a maximum of 5 years at 40 km was assumed. The record of tropospheric total chlorine documented by the World Meteorological Organization (1994) is used to infer Cl_t from the age of the air.

Based on our current knowledge of stratospheric chemistry, the sum of chlorine species measured by the MkIV interferometer supplemented with the other few species discussed above, should account for all of the chlorine. Indeed, Fig. 1 shows a remarkable agreement between predicted and observed total chlorine over most of the altitude range. However there is a striking discrepancy in a layer around 17 km, where ~0.3 ppbv of chlorine is missing. Good agreement between MkIV CCl_y and *in situ* organic chlorine measurements aboard the ER-2 (Elkins et al., 1996) yields a high level of confidence in the ability of MkIV to measure total organic chlorine. Also, for this same September 1993 MkIV data set, Sen et al. (1996) examined the fluorine budget which shares many of the species involved in the chlorine budget, and found very good agreement with model predictions for both fluorine sources and reservoirs. On this basis, we attribute the missing chlorine to the inorganic chlorine family.

The difference between Cl_t and the sum Cl_y+CCl_y is shown in Fig. 2. The error bars are the 1-σ precision propagated errors, and do not include an estimate of systematic errors, which are mainly due to spectroscopic uncertainties. Although these uncertainties are substantial, they are mostly altitude independent and therefore do not detract from the significance of the deficit. Such a feature was not observed in the 1985 ATMOS Spacelab 3 observations (Zander et al., 1992). However, an important difference between the two observations is that the MkIV balloon flight took place in an atmosphere with levels of sulfate aerosols still high after Mt. Pinatubo's eruption in 1991, while the ATMOS experiment flew in a relatively clean atmosphere. The

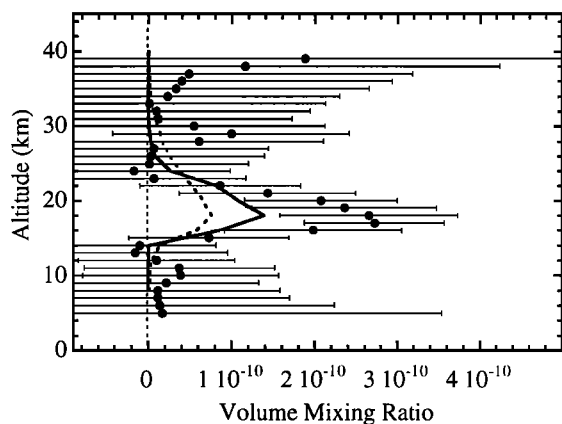


Figure 2. Comparison between MkIV observations of the chlorine deficit (●), and calculated vertical profile of HClO₄ (—). A model calculation which include vertical eddy diffusion is also shown (---).

ATMOS ATLAS-3 mission chlorine retrievals (Zander et al., 1996) and the other MkIV balloon flights made in 1992 and 1993 do not extend to altitudes low enough to detect any discrepancy in the chlorine budget. In the following section, we will speculate that the missing chlorine suggested by the MkIV measurements is held in HClO₄, a species which could be produced on sulfate aerosols.

Perchloric Acid and Sulfate Aerosols

The possibility of HClO₄ formation in the stratosphere was first discussed by Simonaitis et al. (1975). They proposed the following three body reaction:



ClO₃ itself can be formed either from photolysis of Cl₂O₃ or from OClO+O+M (Sander and Friedl, 1995). Both require OClO, which is present at significant levels only in the polar springtime. Thus this process can only contribute to very small amounts of perchloric acid at mid-latitudes. More recently, Prasad and Lee (1994) presented another possibility:

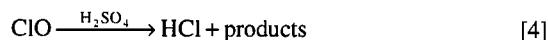
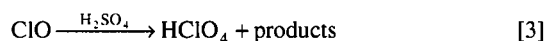


where the ClO·O₃ radical would be formed via reaction of ClO·O₂ with ozone. The stability of ClO·O₂ is itself still subject to discussion (Prasad and Lee, 1994) and the existence of ClO·O₃ is hypothetical.

Martin et al. (1980) obtained measurements of the ClO heterogeneous reactivities on sulfuric acid. Loss of ClO was monitored over the 240–293 K range. The following temperature-dependent uptake reaction probability was derived:

$$\gamma(T) = \exp[-9.361 + (3.22 \pm 1.43)(1000/T - 3.867)] \quad [a]$$

The main chlorine containing product was found to be HCl (accounting for 60–100% of the ClO lost), and, interestingly, small amounts of HClO₄ were also detected (Martin et al., 1979):



Moreover, formation of HCl and perchloric acid was seen from reactions of Cl radicals and Cl₂ molecules on sulfuric acid. It is unclear what mechanism would cause HClO₄ formation in sulfuric acid. To our knowledge, no other measurements of ClO uptake on sulfuric acid have been published (note that preliminary measurements by R. Zhang (private communication) seem to suggest a slower reaction probability). Martin et al. examined the possible significance of HCl formation via [4] for stratospheric chemistry. They concluded that [4] contributes to a slight reduction of the Cl/HCl ratio at 20 km under background aerosol loading conditions. The impact of [3] has not been examined, and is an interesting possibility to consider under volcanic aerosol levels. Recent *ab initio* characterization of perchloric acid (Francisco et al., 1995) have shown that the molecule, under the form HOClO₃, is stable to thermal decomposition. If it appears that under some conditions HClO₄ could be formed in substantial amounts in the stratosphere, we need to examine the possible loss mechanisms of this molecule.

As very little is known about the stratospheric loss processes of HClO₄, we base our considerations on analogies with HCl and HOCl. The [O-H] bond is thermodynamically more stable in HClO₄ than in HOCl, if we use the heat of formation for HClO₄ and ClO₄ calculated by Colussi and Grela (1993). Therefore, we adopted a rate constant for reaction of OH with HClO₄ to be 5

times slower than that with HOCl. Photolysis experiment of concentrated liquid HClO_4 (Huie and Peterson, 1983) suggest slow decomposition of HClO_4 in the near UV and visible, thus its loss by photolysis in the atmosphere is probably negligible and we have chosen it to be equal to the HCl photolysis rate. Alternatively, HClO_4 could be removed by inclusion into sulfate aerosols. We are not aware of any measurements of the solubility of perchloric acid in sulfuric acid solutions, so we estimated its Henry's law constant from basic thermodynamical properties in water (Colussi and Grela, 1993; Karapet'yants and Karapet'yants, 1970) and comparison with HCl solubilities in water and sulfuric acid (Hanson et al., 1994; Clegg and Brimblecombe, 1990). Taking into account the dissociation of HClO_4 to form ClO_4^- in solution, we obtain a Henry's law constant of about $10^6 \text{ M}\cdot\text{atm}^{-1}$ at 200K (compared to $6 \times 10^4 \text{ M}\cdot\text{atm}^{-1}$ for HCl). Thus, less than $10^{-2}\%$ of the HClO_4 will be sequestered in the aerosol phase. However, if we use *ab initio* calculations of the heat of formation of HClO_4 (Francisco et al., 1995), the value obtained for Henry's law would be much higher and a significant fraction of HClO_4 could be in the aerosol phase. Direct laboratory measurements would be necessary to settle this issue.

Model Description

We have implemented the simple HClO_4 chemistry outlined above (using the upper limit of 40% for HClO_4 yield from ClO uptake on sulfuric acid) in a photochemical box model (Allen and Delitsky, 1990). We have assumed HClO_4 to be released to the gas phase, where it is lost by reaction with OH and photolysis. Heterogeneous processes also included are hydrolysis of N_2O_5 and ClONO_2 (Hanson et al., 1994).

Given the large lifetime of HClO_4 (2-10 months in the lower stratosphere), we have performed our calculations for the 3 years following Mt. Pinatubo's eruption in June 1991, thus taking into account the progressive decrease of the aerosol surface area. The surface area evolution as a function of altitude is based on a 2-D model calculation by Tie et al. (1994) at 45°N , which we adjusted to match the aerosol profile measured by the SAGE II satellite close in space and time to the balloon measurement (G. Maddrea and L. Thomason, personal communication). The altitude profiles for O_3 , H_2O , CH_4 have been constrained to the conditions observed by the MkIV balloon instrument on September 25, 1993. Cl_y was taken as the difference between total chlorine, Cl_t , and CCl_y . Transport was not included in the model, but the sensitivity of the results to vertical diffusion was tested.

Model Results / Discussion

The model results show that HClO_4 is produced in a layer between 16 and 22 km (Fig. 2), where most of the aerosol surface area is contained and the temperatures are below 210 K. The altitude and magnitude of the peak depend on the assumption made for ClO reactivity on aerosols, as well as on the loss term. In particular, an exponential dependence on temperature (equation [a]) yields a profile of HClO_4 peaking around 22 km (not shown here). Since the time of the early measurements by Martin et al. (1980), many heterogeneous reactions have been shown to be extremely sensitive to the water content of the sulfuric acid aerosol (Hanson et al., 1994). We have therefore attempted to fit the original measurements of Martin et al., by using a dependence on sulfuric acid weight percent (WH_2SO_4) instead of temperature. We obtained the following expression:

$$\gamma(\text{WH}_2\text{SO}_4) = 10 [3.65 - 0.094 \times \text{WH}_2\text{SO}_4] \quad [\text{b}]$$

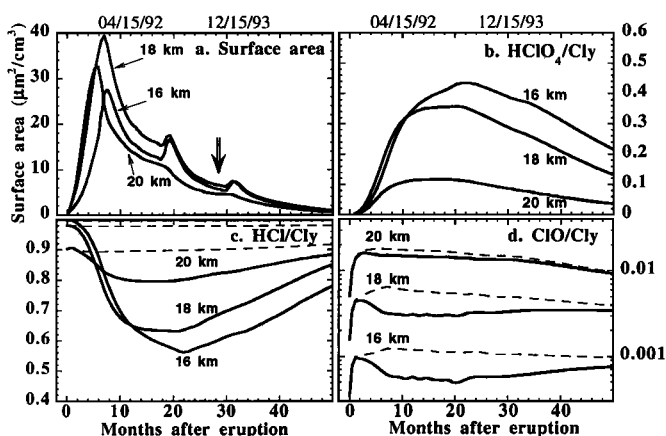


Figure 3. Time dependent box model calculation since Mt. Pinatubo's eruption. (a) Aerosol surface area evolution at 16, 18 and 20 km (2-D model output by Tie et al., 1994). The solid lines represent model calculations including HClO_4 chemistry (see text) for (b) $\text{HClO}_4/\text{Cl}_y$, (c) HCl/Cl_y , and (d) ClO/Cl_y . The dashed lines illustrate the effect standard heterogeneous chemistry only (N_2O_5 and ClONO_2 hydrolysis). The arrow on panel (a) indicates the time of the MkIV balloon flight.

This has the main effect of increasing the uptake coefficient for dilute aerosols found in the lower stratosphere (yielding $\gamma = 0.02$ at 18 km). As can be seen in Fig. 2, the mixing ratio of HClO_4 predicted by the model peaks at 16 km (using [b]), with a shape similar to the observations of missing chlorine, but reaching a lower maximum. Given the uncertainties associated with both the chemistry of HClO_4 and this idealized calculation, we have not attempted to obtain a better match with the observed deficit. Introducing vertical eddy diffusion has the effect of smoothing this profile vertically (dashed line in Fig. 2). A faster rate for $\text{HClO}_4 + \text{OH}$ would decrease the amplitude of the peak in HClO_4 .

Figure 2 illustrates the fact that heterogeneous production of HClO_4 is a possible candidate to account for the missing chlorine inferred from the MkIV measurements. Even though the sticking coefficient for ClO in reaction [3] is small, it could be very effective at producing HClO_4 because of the assumed slow gas-phase loss of this species.

The impact of the rapid increase followed by a slow decrease of aerosol levels as caused by Mt. Pinatubo would be a delayed response of HClO_4 concentrations, as illustrated in Fig. 3. The only time-varying input in our model calculation was the aerosol loading (Fig. 3a). $\text{HClO}_4/\text{Cl}_y$ reaches a maximum of 35-45% 6 months after the peak in surface area, and then slowly decreases through photochemical loss. HCl follows the mirror image of HClO_4 , and is reduced by 45-35% below 18 km. To distinguish the effect of HClO_4 chemistry and the perturbation introduced by N_2O_5 and ClONO_2 hydrolysis, we have represented a model calculation including only standard chemistry (dashed lines). The uptake of ClO on sulfate aerosols has little effect on the relative partitioning of other chlorine species: production of HCl via reaction [4] is slow compared to the $\text{Cl} + \text{CH}_4$ reaction. HClO_4 mainly acts as a temporary sink for inorganic chlorine thereby lowering the amount of Cl_y available for HCl formation. Interestingly, the increase in surface area results in a smaller and less prolonged increase in ClO when HClO_4 chemistry is included (Fig. 3d). Thus, volcanic eruptions such as Mt. Pinatubo's may have the effect of temporarily reducing the available Cl_y for conversion to ClO, thereby rendering ozone molecules less vulnerable to loss via chlorine catalytic cycles.

We have attempted to detect HClO_4 in the stratosphere using the MkIV infra-red spectra, but the large abundance of N_2O and H_2O lines in the region where we would expect to see an absorption feature (Karelin et al., 1975), and the lack of high-resolution spectral information, have not allowed us to clearly prove or disprove the presence of HClO_4 .

Implications / Conclusions

In situ measurements from the ER-2 aircraft of HCl in the lower stratosphere made in 1992 and 1993 have revealed a serious discrepancy in our understanding of the partitioning of inorganic chlorine at mid-latitudes: 30-50% of the inorganic chlorine could not be accounted for by the sum of measured HCl, ClO and inferred steady-state ClONO_2 (Webster et al., 1994). These measurements were made in the northern hemisphere, in the presence of high aerosol loading resulting from Mt. Pinatubo's eruption, and, as evidenced in Fig. 2, could be consistent with heterogeneous formation of HClO_4 .

More recent *in situ* observations by this same instrument indicated a recovery of HCl, with mixing ratios slowly increasing as a function of time as the aerosol loading is decreasing (C. Webster, private communication). This progressive recovery of the *in situ* HCl observations between 15 and 20 km is qualitatively consistent with a slow release of the sequestered Cl_y possibly in the form of perchloric acid, as predicted by the box model calculation.

In this paper, we have proposed that perchloric acid, given certain assumptions on its chemistry, might sequester an important fraction of the inorganic chlorine in the presence of high levels of sulfate aerosols. This hypothesis provides a qualitative explanation for the imbalance in the chlorine budget observed by the MkIV instrument, and might provide a possible explanation for the low HCl aircraft measurements. More robust conclusions await laboratory determinations of the possible production and loss mechanisms outlined in this paper, as well as possible detection of the species in the stratosphere.

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